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THE DETERMINATION OF MALIC AND TARTARIC ACIDS IN THE SAME SOLUTION.

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INTRODUCTION.

The usual method for the determination of tartaric, citric, and malic acids in the same solution is a modification of that proposed by Schmidt and Hiepe.¹ It depends on the precipitation of the acids in the form of calcium salts and on the separation of these by means of their solubility in water and alcohol. The separations obtained in this way are far from sharp and the results are usually unsatisfactory.

It is the purpose of the present paper to present some preliminary notes on a new method for the determination of malic and tartaric acids in the same solution. While the work is far from complete, it is hoped that the publication of the results so far obtained may be of some value and may lead to further researches along the same line.

Walden² first pointed out that when malic and tartaric acids are treated with uranium salts under definite conditions marked increases in their optical rotations are produced. Within certain limits these increased rotations are proportional to the concentration of the acids. These facts have recently been used by Yoder,³ Dunbar and Bacon,⁴ and Dunbar⁵ as the bases of quantitative methods for the determination of malic and tartaric acids when occurring separately. Yoder⁶ suggested that the amounts of these acids present in the same solution may be calculated if some value is determined in

¹ Zts. Anal. Chem., 1882, 21: 534; U. S. Dept. Agr., Bureau of Chemistry Bul. 107, Rev., p. 80.

² Ber. d. chem. Ges., 1897, 30 (3): 2889.

³ J. Ind. Eng. Chem., 1911, 3: 563.

⁴ J. Ind. Eng. Chem., 1911, 3: 826; U. S. Dept. Agr., Bureau of Chemistry Cir. 76.

⁵ U. S. Dept. Agr., Bureau of Chemistry Cir. 106.

⁶ J. Ind. Eng. Chem., 1911, 3: 573.

addition to the rotatory power of the solution after treatment with uranyl acetate. He recommended for this purpose the determination of total acidity. It is obvious that this method is applicable only in cases where malic and tartaric are the only acids present and where these are entirely in the free condition.

In the present experiments advantage is taken of the fact that when oxidized with potassium permanganate in the presence of an excess of alkali malic and tartaric acids, like lactic acid, are converted quantitatively into oxalic acid. This has been shown by Bacon and Dunbar¹ and has been used by them as the basis of a method for the determination of lactic acid in products made from spoiled tomatoes. When malic or tartaric acids are oxidized in this manner, the oxalic acid which is formed may be determined either by precipitation as calcium oxalate or by titration in acid solution with potassium permanganate. The amount of potassium permanganate reduced may also be determined directly by titration. It is unnecessary to point out that the latter procedure can be employed only in the absence of other reducing substances while the former can not be used in the presence of other substances forming oxalic acid on oxidation unless it is possible to separate malic and tartaric acids from these substances before oxidation. That the method is capable of determining malic and tartaric acids separately with considerable accuracy is shown in Tables 1, 2, and 3.

In Table 1 the oxalic acid formed by oxidation was determined gravimetrically; in Table 2 it was titrated in acid solution with potassium permanganate, while in Table 3 the amount of malic or tartaric acid present was calculated indirectly from the amount of potassium permanganate reduced. In all three tables the results marked with a superior figure are from an earlier paper¹ and are introduced here for the sake of completeness. The details of the methods used will be given later.

TABLE 1.—*Determination of malic acid.*

[Oxalic acid determined gravimetrically.]

Acid.	Weight of acid present.	Calcium oxalate $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$.		Weight of acid found.
		Found.	Theory.	
	Gram.	Gram.	Gram.	Gram.
Malic.....	0.25	0.530	0.545	0.243
Do. ¹20	.435	.436	.206
Do. ¹10	.220	.218	.102

¹ U. S. Dept. Agr., Bureau of Chemistry Cir. 78.

TABLE 2.—*Determination of tartaric or malic acid.*

[Oxalic acid titrated with potassium permanganate.]

Acid.	Weight of malic or tartaric acid present.	Weight of oxalic acid found.	Weight of malic or tartaric acid found.
	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>
Tartaric ¹	0.293	0.485	0.289
Do.....	.25	.37	.22
Do.....	.25	.41	.24
Do.....	.25	.36	.21
Malic.....	.25	.47	.247

TABLE 3.—*Determination of malic or tartaric acid.*

[Calculated indirectly from amount of potassium permanganate reduced.]

Acid.	Weight of acid present.	Weight potassium permanga- nate required.	Weight of acid found.
	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>
Malic.....	0.950	2.67	0.942
Do.....	.498	1.39	.493
Do. ¹10	.272	.096
Do. ¹10	.282	.099
Do. ¹10	.301	.106
Tartaric ¹10	.211	.100
Do.....	.250	.55	.26
Do.....	.250	.54	.256
Do.....	.250	.54	.256

¹ Results taken from U. S. Dept. Agr., Bureau of Chemistry Cir. 78.

PRINCIPLE OF THE METHOD.

As has been stated, solutions of both malic and tartaric acids when treated with uranyl acetate under proper conditions show an increased rotation, which, within certain limits, is proportional to the concentration. Both acids also reduce definite amounts of potassium permanganate in alkaline solution and form oxalic acid quantitatively. Hence it is possible to calculate the amounts of malic and tartaric acids in a solution, knowing the total change in rotation of the solution on treatment with uranyl acetate, and also either the amount of potassium permanganate reduced or the amount of oxalic acid formed when the solution is oxidized in alkaline solution.

EFFECT OF URANYL ACETATE ON THE ROTATIONS.

It has been shown by Dunbar and Bacon ¹ that a solution containing 1 gram of malic acid in 100 cc will rotate -27.77° V. when treated with uranyl acetate under proper conditions. In another

¹ U. S. Dept. Agr., Bureau of Chemistry Cir. 76; J. Ind. Eng. Chem., 1911, 3: 826.

publication¹ on the determination of tartaric acid, it has also been shown that a solution containing 1 gram of tartaric acid in 100 cc will when treated with uranyl acetate under proper conditions produce a rotation of $+19.61^{\circ}$ V. In a solution containing both acids, these changes in rotation are produced by each independently of the other.

REACTION OF MALIC AND TARTARIC ACIDS WITH POTASSIUM PERMANGANATE.

When malic acid is oxidized with potassium permanganate in the presence of an excess of alkali, the following reaction occurs:

(1) $C_4H_6O_5 + 4KMnO_4 = 2H_2C_2O_4 + 2MnO_2 + 2K_2MnO_4 + H_2O$. On acidifying this mixture, as is done when the total amount of reduced permanganate is to be determined, oxalic acid is further oxidized by potassium permanganate according to the following equation:

(2) $5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + 8H_2O + K_2SO_4 + 2MnSO_4$. One gram of potassium permanganate is equivalent to 0.353 gram of malic acid or 1 gram of malic acid equals 2.8297 grams of potassium permanganate. One gram of oxalic acid, $C_2H_2O_4 + 2H_2O$, is equivalent to 0.526 gram of malic acid, or 1 gram of malic acid equals 1.90 grams of oxalic acid.

When tartaric acid is oxidized in the same manner the equation is:

(1) $2C_4H_6O_6 + 6KMnO_4 = 4H_2C_2O_4 + 3K_2MnO_4 + 3MnO_2 + 2H_2O$. On acidifying, the oxalic acid is further oxidized as shown in equation (2). One gram of potassium permanganate is equivalent to 0.475 gram of tartaric acid, or 1 gram of tartaric acid equals 2.1062 grams of potassium permanganate. One gram of oxalic acid equals 0.595 gram of tartaric acid, or 1 gram of tartaric acid equals 1.68 grams of oxalic acid.

CALCULATION OF EQUATIONS.

Bearing in mind the rotations of uranium-malic and uranium-tartaric solutions containing 1 gram of acid per 100 cc and also the permanganate equivalent of these acids, the equations for calculating the amounts of malic and tartaric acids from the total change in rotation and the amount of potassium permanganate reduced are deduced as follows:

Let x = grams malic acid in 100 cc.

y = grams tartaric acid in 100 cc.

a = polarization in $^{\circ}$ V. of the solution in a 200 mm tube after treatment with uranyl acetate.

b = grams of potassium permanganate ($KMnO_4$) required to oxidize the acids in 100 cc.

¹ Dunbar, U. S. Dept. Agr., Bureau of Chemistry Cir. 106.

$$\text{Then } -27.77x + 19.61y = a \quad (1)$$

$$\text{and } 2.8297x + 2.1062y = b \quad (2)$$

Solving for x and y , the following equations are obtained:

$$x = -0.0185a + 0.1720b$$

$$y = 0.0248a + 0.2436b$$

The equations for calculating the amounts of malic and tartaric acids from the total change in rotation and the total amount of oxalic acid formed are deduced as follows:

Let x = grams malic acid in 100 cc.

y = grams tartaric acid in 100 cc.

a = polarization of the solution in $^{\circ}\text{V}$. in a 200 mm tube after treatment with uranyl acetate.

c = grams of oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 + 2\text{H}_2\text{O}$) formed by oxidation of the acids in 100 cc.

$$\text{Then } -27.77x + 19.61y = a \quad (1)$$

$$1.90x + 1.68y = c \quad (2)$$

Solving for x and y —

$$x = -0.020a + 0.233c$$

$$y = 0.023a + 0.331c$$

DETAILS OF THE METHOD.

DETERMINATION OF THE ROTATION.

1. Measure 85 cc of the solution under examination into a 100 cc graduated flask, render the solution slightly alkaline to litmus paper with sodium hydroxid, add 5 grams of sodium acetate and shake until dissolved. Reacidify the solution to litmus paper with a strong solution of citric acid, adding a slight excess of the acid, cool to room temperature and dilute to 100 cc. Treat about 30 cc of this solution with powdered uranyl acetate, transfer to a suitable container and shake for 3 hours with a mechanical shaker. Add enough uranyl acetate so that a small amount remains undissolved after 3 hours shaking; from 2 to 3 grams are usually sufficient. If the uranium salt dissolves, more must be added. Filter through a folded filter and polarize if possible in a 200 mm tube. Then agitate the solution for an hour longer with uranyl acetate and again polarize to determine whether a maximum rotation has been obtained. Calculate the reading in degrees Ventzke to the basis of the original solution and designate as (1).

2. Treat about 50 cc of the original solution with dry powdered normal lead acetate until no further precipitation results; avoid excess of the precipitant. A centrifuge can be used to advantage in settling the precipitate. Filter through a folded filter and test the filtrate with a small crystal of lead acetate to determine whether

precipitation is complete. Remove the excess of lead with powdered anhydrous sodium sulphate, filter until clear and polarize in a 200 mm tube. Designate this reading as (2).

Polarize at room temperature with white light, taking care that all solutions are polarized at the same temperature. Make at least six readings on each solution and take the average of these. Calculate all readings to the basis of a 200 mm tube. The algebraic difference between (1) and (2) in degrees Ventzke will give the combined effect of the rotations of the uranium complexes of both malic and tartaric acids. In the absence of optically active substances other than malic and tartaric acids reading (2) need not be made.

DETERMINATION OF THE AMOUNT OF POTASSIUM PERMANGANATE REDUCED.

In the absence of any substances other than malic and tartaric acids which are capable of reducing potassium permanganate, the amount of permanganate reduced is determined as follows:

Render alkaline with sodium hydroxid a measured portion of the solution containing 0.2 to 0.5 gram of total malic and tartaric acids and add an excess of about 3 grams of the alkali. Treat with 50 cc of 1.5 per cent potassium permanganate and heat on the steam bath at 100° C. for one-half hour. At the end of that time the solution should have a decided blue-black or purple color. If the solution turns green or colorless above a layer of brown precipitate at any time during the course of the oxidation more standard permanganate in measured portions must be added until the blue-black or purple color remains throughout a half-hour period of heating. The oxidation is then complete. Acidify the hot solution with about 50 cc of 10 per cent sulphuric acid and run in standard oxalic acid (5 per cent is convenient) from a burette until the solution is colorless. Titrate back any slight excess of oxalic acid with 1.5 per cent permanganate until a permanent pink color is obtained. Calculate the total weight of permanganate used in the oxidation by subtracting the permanganate equivalent of the oxalic acid used from the total amount of permanganate added.

DETERMINATION OF THE OXALIC ACID FORMED.

In the presence of other substances which reduce potassium permanganate but do not form oxalic acid the procedure is as follows:

Oxidize the solution with alkaline potassium permanganate in the manner described above. A standard solution of permanganate need not be used in this case, but an approximately 1.5 per cent solution is convenient. Cool the blue-black or purple alkaline solution and treat with hydrogen peroxid until the excess of potassium

permanganate is destroyed and the solution is colorless except for a brown precipitate. Transfer the resulting solution with the suspended precipitate to a graduated flask of any convenient size, dilute to the mark, and mix well. Filter through a folded filter without washing and pipette the largest possible aliquot of the clear filtrate into a beaker; strongly acidify with about 50 cc of 10 per cent sulphuric acid, boil vigorously for some time to remove the excess of hydrogen peroxid, and titrate hot with standard permanganate to a faint pink color. One cc of 1.5 per cent potassium permanganate is equivalent to 0.0299 gram of oxalic acid, $C_2H_2O_4 \cdot 2H_2O$. The oxalic acid in the solution may also be determined by precipitation as calcium oxalate in the usual manner. In this case the aliquot portion of the filtrate which is used is acidified slightly with acetic acid and the oxalic acid is precipitated with calcium acetate.

In fruit juices and solutions containing sugars, add about three volumes of 95 per cent alcohol to 50 cc of the solution and precipitate the mixed acids with normal lead acetate. Collect the precipitate (conveniently with a centrifuge), wash with 80 per cent alcohol until free from sugars, and decompose with dilute sulphuric acid. Filter off the precipitate of lead sulphate, remove the alcohol by evaporation, and oxidize the acids in the solution as described above.

Calculate the total rotation and the amount of potassium permanganate reduced or of oxalic acid formed to the basis of 100 cc of the original solution and substitute the values so obtained in the proper equation, taking care to preserve the algebraic sign of the rotation.

DISCUSSION OF RESULTS.

The methods suggested above for the determination of malic and tartaric acids have been applied to a number of aqueous solutions containing amounts of the acids which were unknown to the analyst and also to ciders containing added tartaric acid. The accuracy of the methods may be judged by referring to Tables 4 and 5, in which the results are collected.

The last two determinations recorded in Table 4 were made on ciders containing added tartaric acid. The other determinations shown in this table were made on aqueous solutions. In this table the total amount of potassium permanganate reduced was determined in all cases. In the two determinations recorded in Table 5, which were made on apple cider, the amounts of oxalic acid formed were determined directly. Where cider was used for the determinations, the amount of malic acid contained therein was determined by titration and by the uranyl acetate method before the addition of tartaric acid.

TABLE 4.—*Determination of malic and tartaric acids.*

[Potassium permanganate determined.]

Malic acid present (grams per 100 cc.).	Tartaric acid present (grams per 100 cc.).	Rotation of acids after treatment with uranyl acetate (original dilution).	Potassium permanganate reduced by acids in 100 cc.	Malic acid found (grams per 100 cc.).	Tartaric acid found (grams per 100 cc.).
		°V.	Grams.		
0.46	1.96	+24.3	5.40	0.48	1.89
.83	.60	—11.8	3.54	.83	.57
.47	.98	+ 7.3	3.34	.44	.99
.59	.74	— 1.6	3.21	.58	.74
.24	1.24	+17.5	3.22	.23	1.22
1.52	.62	— 1.8	2.03	.51	.63
1.43	.51	— 9.2	2.43	.55	.45

¹ Determinations on ciders containing added tartaric acid.TABLE 5.—*Determination of malic and tartaric acids.*

[Oxalic acid determined.]

Malic acid present (grams per 100 cc.).	Tartaric acid present (grams per 100 cc.).	Rotation of acids after treatment with uranyl acetate (original dilution).	Oxalic acid formed from acids in 100 cc.	Malic acid found (grams per 100 cc.).	Tartaric acid found (grams per 100 cc.).
		°V.	Grams.		
0.43	0.51	—9.2	1.42	0.51	0.68
.60	.59	—5.2	2.15	.60	.59

Attention is again called to the fact that the presence of substances which form oxalic acid on oxidation with alkaline potassium permanganate, and which can not be separated from malic and tartaric acids by precipitation with lead acetate, interferes with the determination.

SUMMARY.

The method suggested herein for the determination of malic and tartaric acids depends on the following facts:

(1) That the optical rotations of both acids are increased independently of each other when treated with uranyl acetate under definite conditions.

(2) That both acids may be oxidized quantitatively to oxalic acid by heating with potassium permanganate in alkaline solution.

Knowing the total rotation produced by these acids on treatment with uranyl acetate and either the amount of oxalic formed by oxidation or the amount of potassium permanganate reduced, it is possible to calculate the amounts of malic and tartaric acids present in a solution. The presence of substances which form oxalic acid on oxidation and which can not be removed before treatment with potassium permanganate interferes with the method.